SUPERCONDUCTIVITY PROPERTIES OF EVAPORATED THIN TIN FILMS WITH METALLIC BACKING

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Submitted in partial fulfillment of
the requirements for the degree of

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ABSTRACT

Thin film specimens were produced as free as possible from defects, and investigations of the critical current as function of temperature were made on tin films evaporated on glass, in some cases with copper or aluminum backing. It was found that the metallic backing had a significant effect on the critical current in the region around the transition temperature for pure tin (3.71°K). At temperatures slightly higher than the value at which there was a sudden rise in critical current, the tin films with metallic backing appeared superconductive, although there was no change in critical current with temperature. Values of this apparent transition temperature for tin were found to be 3.04°K for copper backing and 3.44°K for aluminum backing. In addition at the lamda point (2.186°K) there was found to be no substantial jump in the critical current for the specimens with copper or aluminum backing.

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1. Introduction.

At the time when Kamerlingh Onnes first discovered superconductivity in 1911, no complete theory of metals existed. Since then satisfactory qualitative explanations for most metallic phenomena have been found, but superconductivity has remained anomalous. Recent developments have made it possible to correlate some of the properties of superconductors, and thus to distinguish between fundamental and secondary features.

The first problem in any experiment on superconductivity is to prepare a suitable specimen. The specimen must be as free as possible from any defects which may introduce secondary features and thus confuse observation of what is described as ideal behavior. As explained in Shoenberg[1] chemical purity, including freedom from dissolved gasses, and freedom from internal stresses are essential.

The first characteristic property of superconductors is the disappearance of electrical resistance below a certain temperature called the transition temperature. When a steadily increasing current is passed through a superconductor, the field associated with the current eventually becomes great enough to destroy the superconductivity. The maximum current the superconductor can carry without becoming resistive is called the critical current.

In thin films the current is probably concentrated in the edges and the current distribution function has not yet been determined.[2] To further complicate this problem fuzzy edges are produced when a superconductive material such as tin is evaporated directly onto glass. It is

[1] D. Shoenberg, Superconductivity, Cambridge University Press, 1952, pp. 7-12.

[2] Ibid., pp. 174-178.

thought that better edges are produced when the superconductive material is evaporated on a metallic backing than directly on a glass flat. It is well known that the electrical properties of evaporated thin films depend markedly on the cleanliness of the conditions of deposition; in particular, reproducible results are obtained only if the vacuum is at least of the order 10^{-6}mm. One purpose of this project was to construct the apparatus for producing clean evaporated thin films. Another purpose was to investigate the critical currents for tin evaporated directed onto glass flats and onto backings of copper or aluminum which had been first plated on the glass flats. It is hoped that this work will aid future investigators in making better thin films for superconductivity experiments and explain some of the phenomena associated with using metallic backings for the superconducting material.

2. Theory of film formation.

The atoms, which constitute the vapor phase of the substance being evaporated, collide with the atoms of the substrate with a velocity which depends among other things upon the temperature of the furnace. Much of this kinetic energy is immediately given up to the atoms of the substrate which is organized in a somewhat random manner in the case of glass. For an atom to remain in contact with the substrate it is necessary that the binding energy be greater than its thermal energy, otherwise it re-evaporates. The essential point governing the film behavior is that in general the binding force necessary to hold an atom in a fixed position on the substrate is much greater than the force necessary to prevent evaporation.

We are thus led to consider the two quantities; the heat of evaporation from the surface or the energy necessary for a particular atom to leave the substrate and the heat of sublimation which is that energy required for an atom to leave a collection of like atoms. Now if the heat of evaporation were large compared to the heat of sublimation, we should be able to uniformly coat a substrate with a monatomic layer of metal. This case rarely occurs; when metals are condensed onto glass the reverse happens. The cohesive forces between metal atoms are much stronger than the adhesive forces between the atoms and the glass so that the atoms aggregate until a stable configuration results.

It is known that films which are non-continuous in the sense that they are not electrical conductors are further exposed to metallic vapor and their thickness increased beyond a critical range, they do become electrically conducting. This very rapid increase in conductivity is not surprising since the processes of condensation and migration are quite random, and thus the thin film has a high degree of uniformity insofar as the distribu-

tion of particles is concerned and upon addition of further atoms the film as a whole will more closely approach electrical continuity, i.e., the gaps between crystals become uniformly narrower. Finally the addition of a relatively small amount of metal will close a large number of gaps almost simultaneously so that where previously there were no conducting paths across the film, there rather suddenly appear a large number.

The cleanliness of the substrate is an important factor in the properties of thin films. Both water vapor and gas play important roles as contaminants on various substrate material. It has been shown that if evaporation is done at pressure of 10^{-6}mm a certain amount of spontaneous cleaning of these contaminants takes place and the adherance of metal films to glass improves.[3] If the substate is maintained at reduced temperature, agglomeration is sharply reduced since the metallic atoms more quickly lose their energy to the substrate and fall below the activation level for migration.

Film structure is also found to depend upon pressure over a considerable range. At higher pressures, where the mean free path is small compared to the distance over which the metal atoms travel, these atoms arrive at the substate after diffusing through this residual atmosphere. Many are scattered to the side and rear and this together with straggling results in a decreased deposition rate. Accordingly the agglomeration is increased. Although perhaps not too convincing, there is a suggestion that once the pressure is reduced so that the mean free path becomes greater than the distance from furnace to substrate, there is little change in film structure, probably for the reason above.

[3]M. S. Blois, Jr., Thesis, Stanford University, 1951.

3. Evaporation technique.

The first step in the preparation of the thin films was to obtain a clean surface on the glass flat. The glass flat was placed in a holder and immersed in a solution of boiling distilled water and a special detergent "Kwip", and was swabbed with cotton. The glass flat was then removed and rinsed by pouring boiling distilled water over it. It was then sprayed with alcohol and dried with ordinary paper towels, care being taken not to touch the glass flat. The purpose of this cleaning was not so much to remove all specks of dust or other inorganic matter, as to avoid contamination by a monolayer of grease or oil which would prevent the metal atoms from coming into proper contact with the glass. After cleaning, copper wires were soldered with indium onto the glass for electrical contacts used to determine evaporation rate and resistance of material deposited during evaporation. The glass flat was now ready to be put into the evaporation apparatus.

The essential elements of the apparatus are shown in Fig. 1, 2 and 3 and consist of a flat steel plate to which a glass jar is ground with a neoprene seal and a small amount of vacuum grease and a top flat aluminum plate which is ground in the same manner to the jar, a vacuum pump capable of producing a pressure of 10^{-8}mm., copper rods used as supports and electrodes for the tantalum boats, central liquid air trap for cooling and supporting the sample glass flat, side liquid air trap for cooling aluminum plate inside system, water cooling coils around tantalum boats to prevent plates from becoming too hot, and a shutter which prevents substances from striking glass flats before evaporation. On the top aluminum plate there is an ionization gage tube (10^{-3}mm. to 10^{-9}mm. range), and a Stupakoff connection for electrical measurements.

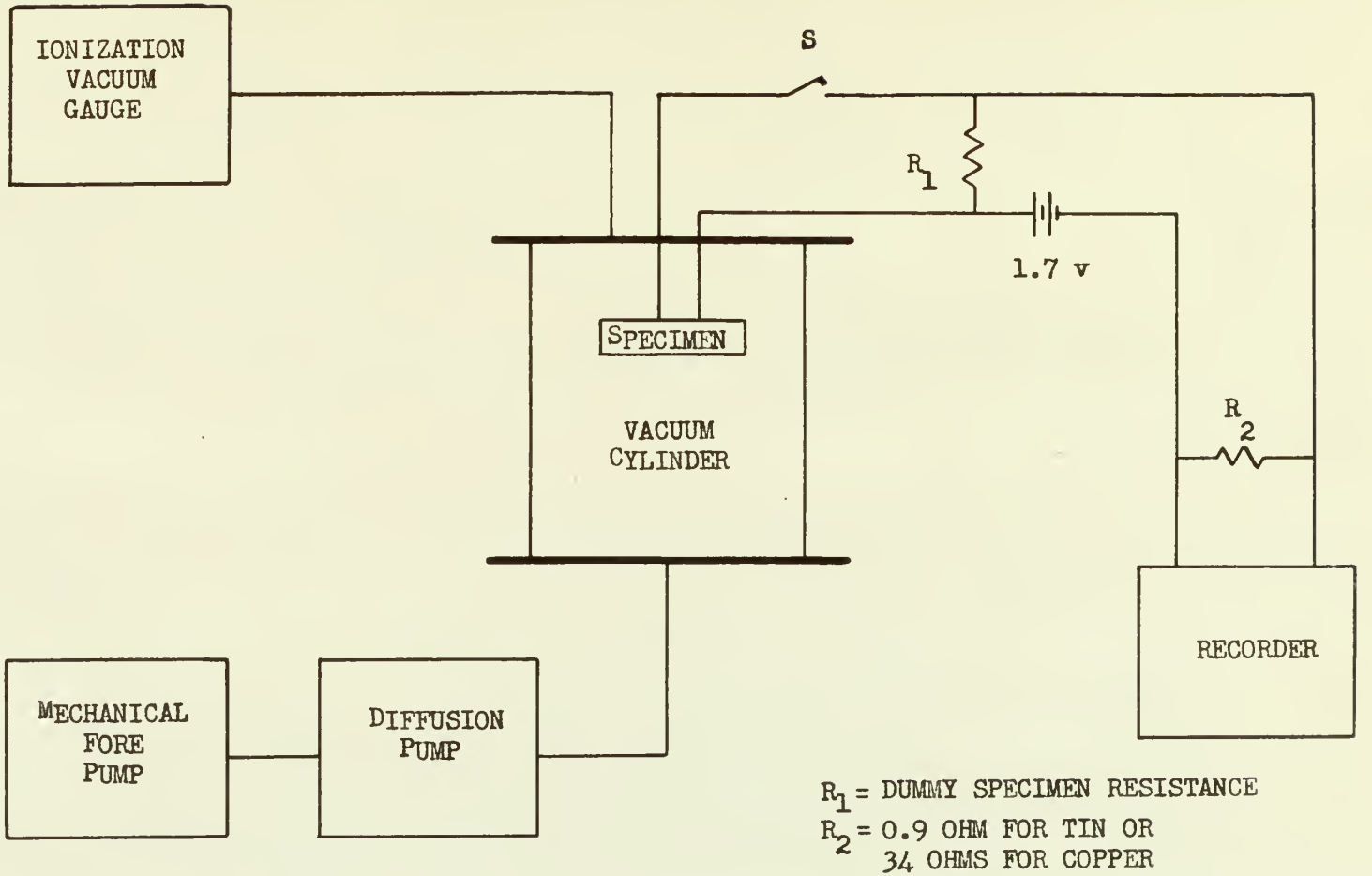


FIGURE 1

FUNCTIONAL BLOCK DIAGRAM FOR EVAPORIZATION OF THIN FILMS

Figure 2

Figure 2

General View of the Evaporating Equipment

This view shows the evaporating equipment with the Kinney Mechanical Fore Pump, Consolidated Vacuum Corporation MCF-300 Diffusion Vacuum Pump, the Vacuum Cylinder, and the Varian Associates Graphic Recorder Model G-10. Evaporation controls are on the left side of the panel; Ionization Vacuum Gauge Type DPA-38 is directly below the recorder.

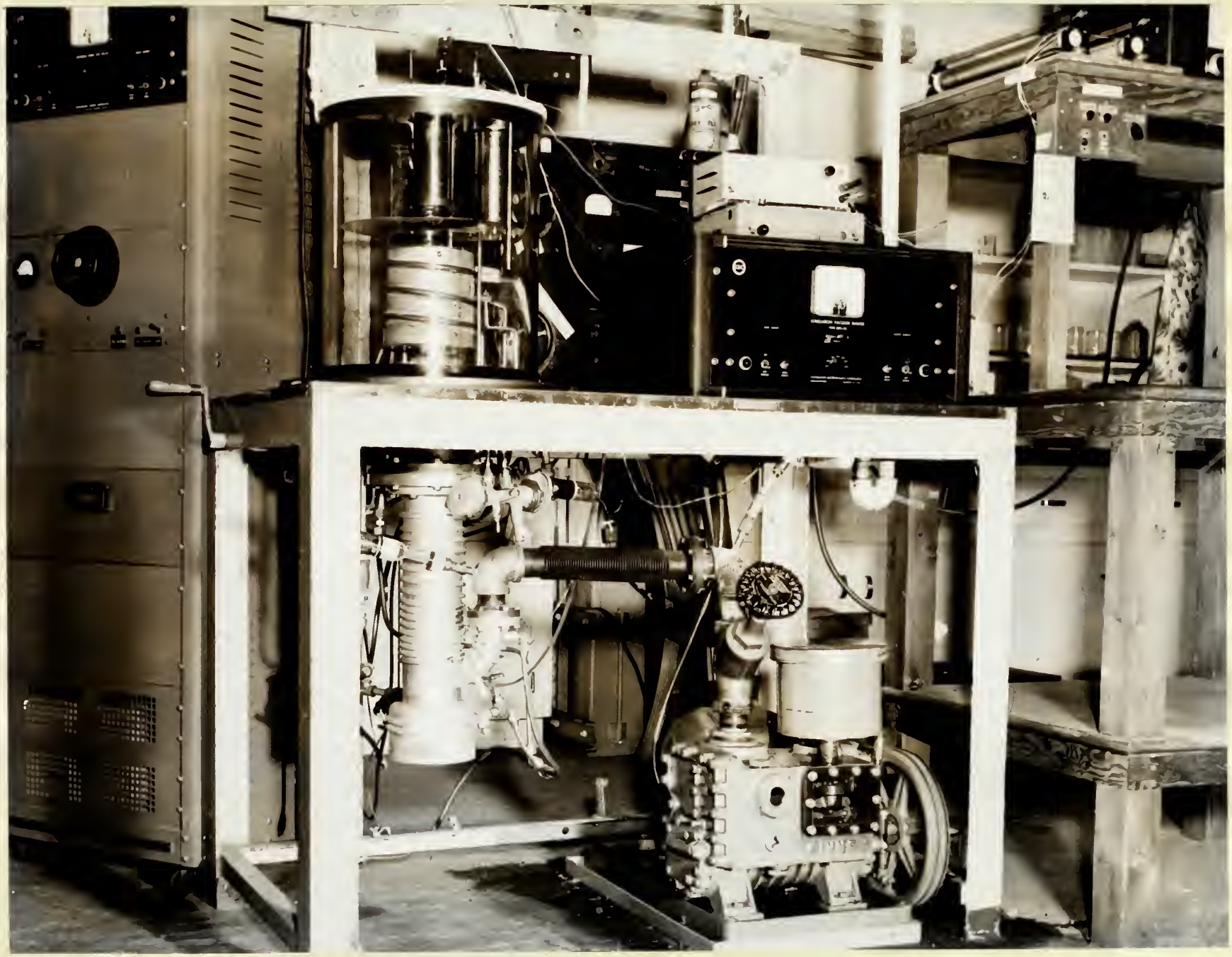
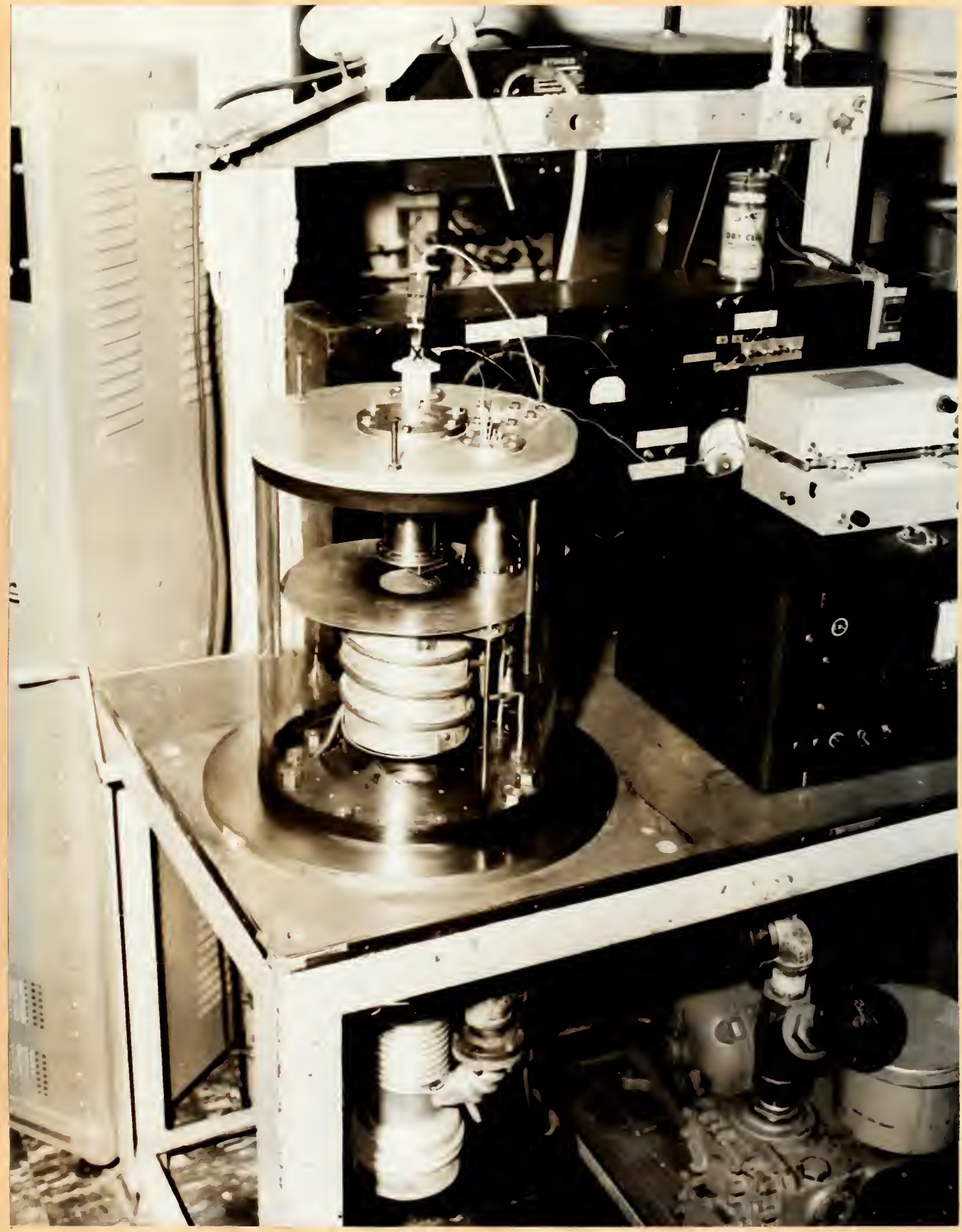


Figure 3-

Figure 3

The Vacuum Cylinder

A close-up view of the internal set-up inside the vacuum cylinder.



Two razor blades $\frac{1}{4}$" long and separated by approximately 50 microns are cemented to a flat plate and are placed in contact with the cleaned glass flat which is cemented on a round plate. This combination is secured to the bottom of the central liquid air trap. The copper wires soldered on the glass are connected through the Stupakoff connector. Either 60 or 300 mg. of tin are placed in one tantalum boat and a small amount of copper or aluminum is placed in the other boat. The top plate is now placed in position. A Varian Associates Graphic Recorder, Model G-10 is connected across the specimen by means of the Stupakoff connector. The system is pumped down and is outgassed by turning the furnace and heating a wire connected between two copper electrodes. The furnace is shut down and liquid air is poured into the traps and allowed to cool the specimen down and lower the pressure. At a pressure range of 5×10^{-8} to 1×10^{-7} mm., the shutter is opened from outside the system, water is allowed to flow around cooling coils, and the furnace which is now connected to the boat containing either the copper or aluminum is turned on. The furnace is left on until approximately 1,000 ohms of metal as registered on the recorder have been evaporated on the glass and then is immediately shut down. The furnace leads are quickly shifted to the boat containing the tin and then a set amount of tin is evaporated out. The system is then shut down and the specimen allowed to warm up to room temperature. The specimen is then removed from the system and the thin film inspected under a 430X microscope.

The films which were made by evaporating tin directly onto the glass did not show as clean straight edges as those which had copper or aluminum evaporated on the glass first. Only those specimens which did not show any flaws under microscopic inspection were used in the DC critical measurements.

It was observed that the resistance of all specimens, regardless of backing material or slit width, decreased by a ratio of three from the value at room temperature to the value at liquid air temperature ($70^{\circ}K$). However, the ratio of resistance at room temperature to the resistance at liquid helium temperature ($4.2^{\circ}K$) ranged from values of 5 to 14 for different specimens. These observations can be explained in part if one considers the resistivity of a metal containing imperfections such as vacancies, interstitials, and impurity atoms as the sum of the resistivity caused by thermal motion of the lattice and the resistivity caused by the imperfection. At high temperatures the resistivity due to the thermal motion predominates and the resistance is therefore independent of the specimen impurities. However as the temperature approaches zero the resistivity due to thermal motion vanishes and the residual resistance may vary from specimen to specimen.[4]

[4]C. Kittel, Introduction to Solid State Physics, John Wiley & Sons, Inc., New York, 1954, pp. 266-267.

4. Experimental procedure.

The superconductivity characteristics of the specimens were investigated by determining the direct current required to cause a voltage drop across the specimen at a particular temperature. This voltage drop indicated the change from the superconducting state to the resistive state.

The specimens were mounted in a holder which was fitted with lead strips to insure electrical contact between the external measuring instruments and the specimen. A variable direct-current supply was used to apply the current to the specimens and an oscilloscope provided a visual presentation of the voltage drop across specimens when the phase change occurred.

The cryostat, specimen, and specimen holder were precooled with liquid air prior to filling the cryostat with liquid helium. The loaded cryostat was allowed to reach temperature equilibrium, as indicated by the cessation of boiling, and the resistance of the specimen at atmospheric pressure (4.2 ^{o}K) was determined. The pressure was then decreased slowly until the specimen became superconducting.

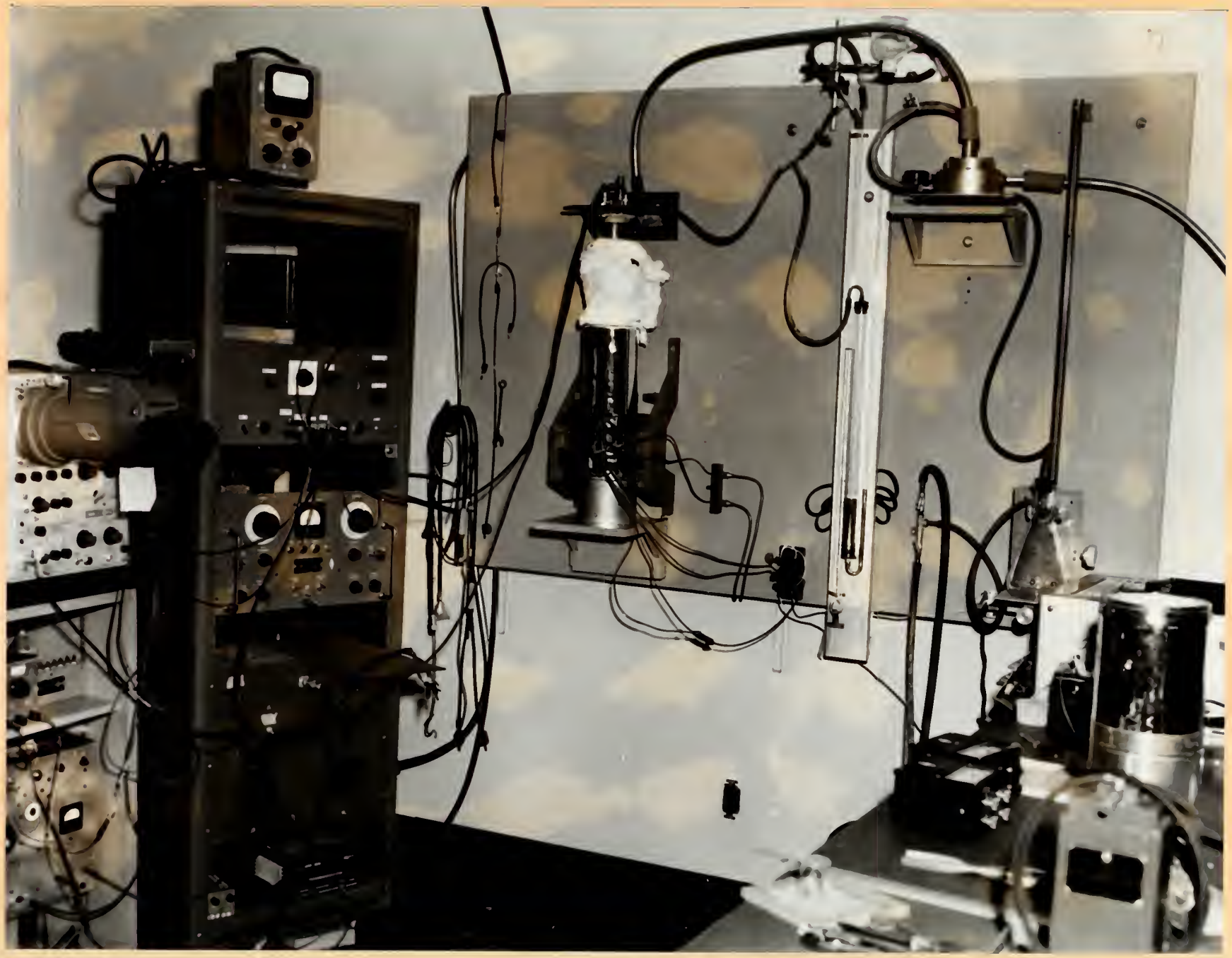
After the specimen became superconducting a direct current was applied to the specimen and the current required to cause the phase change to the resistive state was measured by observing the current value when the oscilloscope trace indicated a change in the voltage across the specimen or when the "tailbiter" cut off the current. This procedure was repeated for different values of temperature. The pressure was always decreased between readings in order to assist in reaching and maintaining temperature equilibrium, and in no case was the specimen allowed to warm up during a run.

Figure 4

Figure 4

General View of the Electrical Measuring Equipment

The critical current vs temperature readings were obtained through the use of a cryostat, oscilloscope, variable direct current supply, current meter, and a pressure apparatus for temperature variation.



5. Results.

An examination of the data accumulated and of Figs. 5 through 12 indicates that a backing of aluminum or copper has a definite effect on the critical current.

One effect of the backing material was the practical disappearance of the critical current jump at the lamda point (2.186°K). In the case of no backing a pronounced jump was observed but in no case was a substantial jump present with any amount of backing material used. The jump in critical current is due to the fact that helium changes phase at the lamda point and becomes about ten thousand times as good a thermal conductor. The heat being generated in the resistive regions of the specimen is transferred more rapidly to the helium at temperatures lower than the lamda point and therefore the specimen requires larger currents to switch to the resistive state. However with metallic backings it is believed that the backing itself acts as an excellent heat conductor and thereby eliminates the jump at the lamda point.

With backing material it was observed that curves of the DC-critical current as a function of temperature flattened out at the higher temperatures. As the temperature decreased, the slopes approached those of the specimens without backing. The flattening-out portion of the backing material curves is not understood but perhaps is due to secondary effect of an alloying material produced during the evaporation.

It was found that the tin without backing material went superconducting at 3.70°K which is in agreement with Shoenberg's value of 3.71°K.[5] However for specimens with copper backing this temperature was found to be 3.04°K and with aluminum 3.44°K. These temperatures for the specimens

[5]Shoenberg, op.cit., p. 224.

with backing material were taken at the apparent transition temperature, the point of the first sudden rise in critical current with temperature. At temperatures lower than this apparent transition value the specimens acted similar to those without backing. At higher temperatures than the apparent transition the specimens with backing had some indication of superconductivity but the critical current remained constant with reduction in temperature. The exact temperature where the first trace of superconductivity took place was not determined.

The apparent transition temperatures observed for the tin with backing material leads to two surprising results. Firstly, although there is no universal rule as to how transition temperature depends on composition, it is more often the case that the transition temperature of the pure superconducting element is increased by the addition of a non-superconducting component.[6] Therefore if it is assumed that the strange behavior at temperatures higher than apparent transition are due to an alloying effect, it must be concluded that copper and aluminum when alloyed with tin act just the opposite as expected and lower the transition temperature. Secondly, it might have been assumed that an increased amount of deposition of tin on the backing material would tend to have the apparent transition temperature of tin approach the true transition temperature of the pure bulk material. However in the case of either 60 or 300 mg. of tin evaporated onto the same amount of copper backing, the apparent transition temperature remained constant. It may be hypothesized that there is a thickness of tin which when evaporated on a backing material would yield results approaching that of the bulk material, and further work into this area to find a critical thickness might yield some interesting

[6]Shoenberg, op.cit., pp.37-47.

results.

It was seen that aluminum had a lesser effect than copper backings at the higher temperatures and this might suggest aluminum as a better backing material. It has been known for a long time that aluminum evaporated onto glass has good adherance and smooth structure due to an additional binding force between the metal and the substrate through a layer of absorbed oxygen existing on the substrate prior to evaporation.[7] Copper films deposited under the same conditions as aluminum would probably show more agglomeration. It is therefore thought that the tin evaporated onto the copper would have more noticeable alloying effects than when evaporated onto the aluminum which had formed very small particles upon plating onto the glass.

The authors wish to express their appreciation to Professors J. N. Cooper and E. C. Crittenden, Jr. of the U. S. Naval Postgraduate School for their friendly guidance and assistance in this project.

Further acknowledgement is made to Mr. K. C. Smith for his valuable aid given in the construction of the apparatus.

[7] Blois, op.cit.

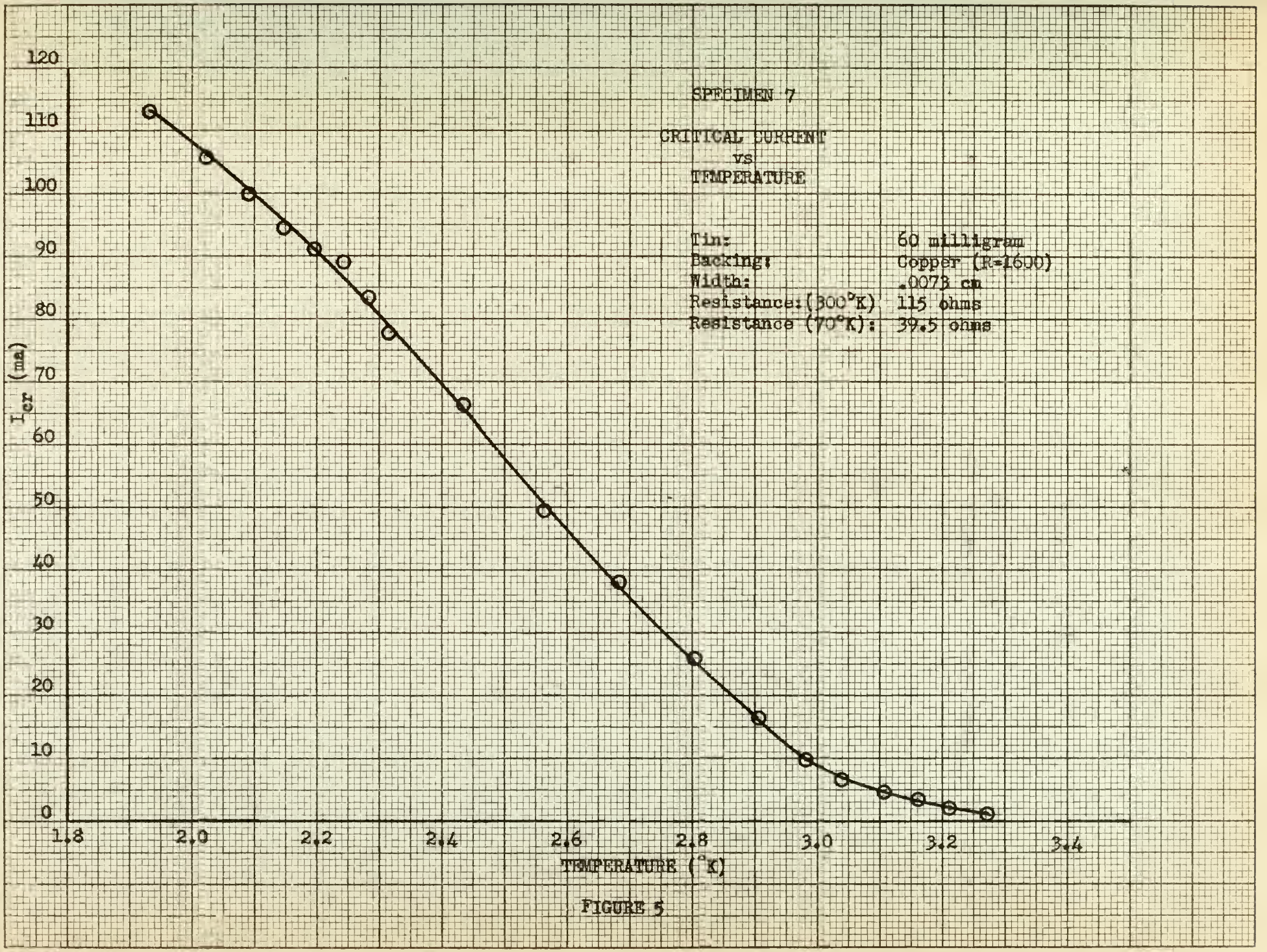

SPECIMEN 7
CRITICAL CURRENT
vs
TEMPERATURE
Tin: 60 milligram
Backing: Copper (R=1600)
Width: .0073 cm
Resistance: (300°K) 115 ohms
Resistance (70°K): 39.5 ohms
I_{cr} (ma)
120
110
100
90
80
70
60
50
40
30
20
10
0
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
TEMPERATURE (°K)

FIGURE 5

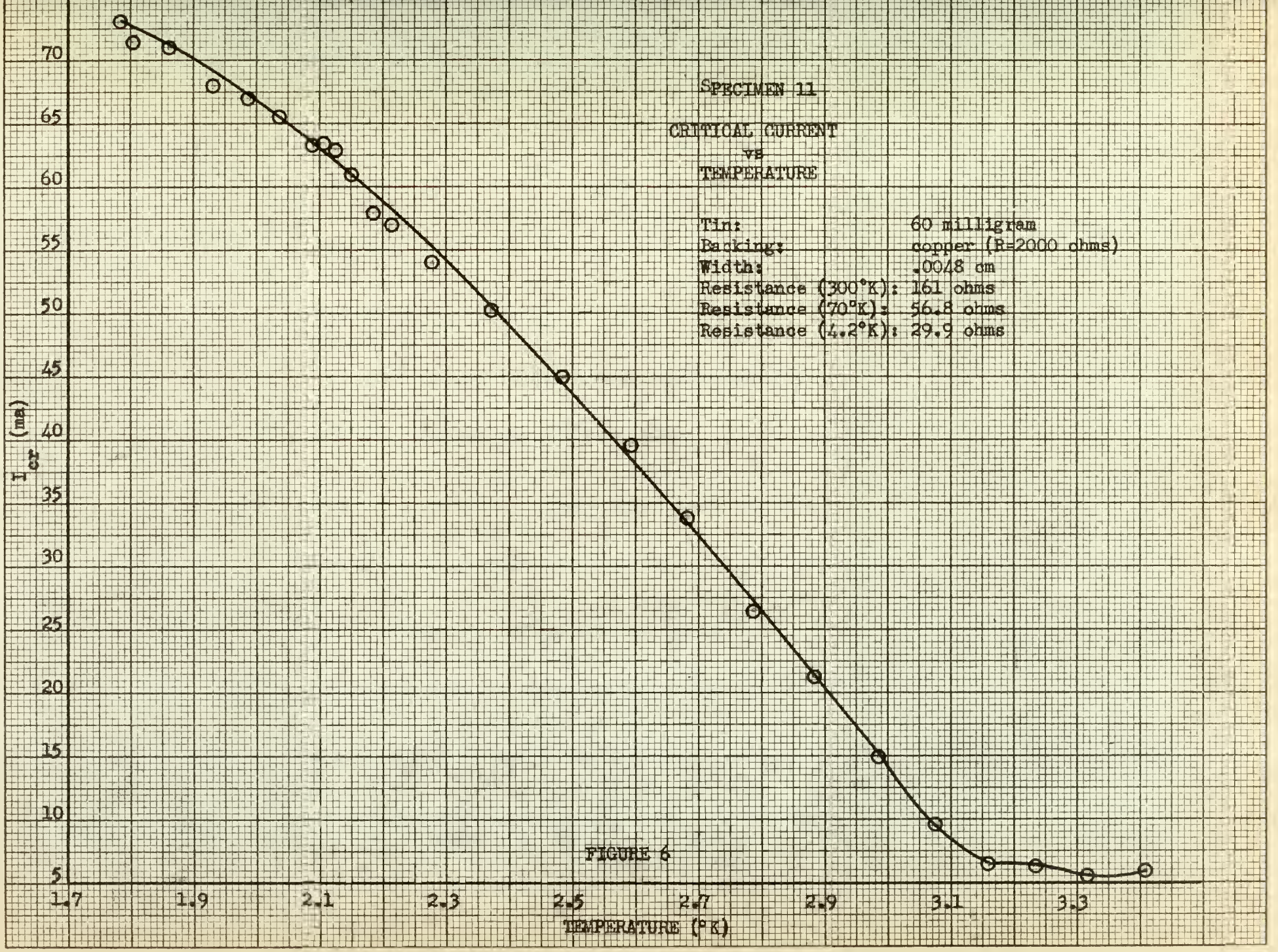

SPECIMEN 11
CRITICAL CURRENT
vs
TEMPERATURE
Tin: 60 milligram
Backing: copper (R=2000 ohms)
Width: .0048 cm
Resistance (300°K): 161 ohms
Resistance (70°K): 56.8 ohms
Resistance (4.2°K): 29.9 ohms
I_c (ma)
70
65
60
55
50
45
40
35
30
25
20
15
10
5
1.7
1.9
2.1
2.3
2.5
2.7
2.9
3.1
3.3
TEMPERATURE (°K)

FIGURE 6

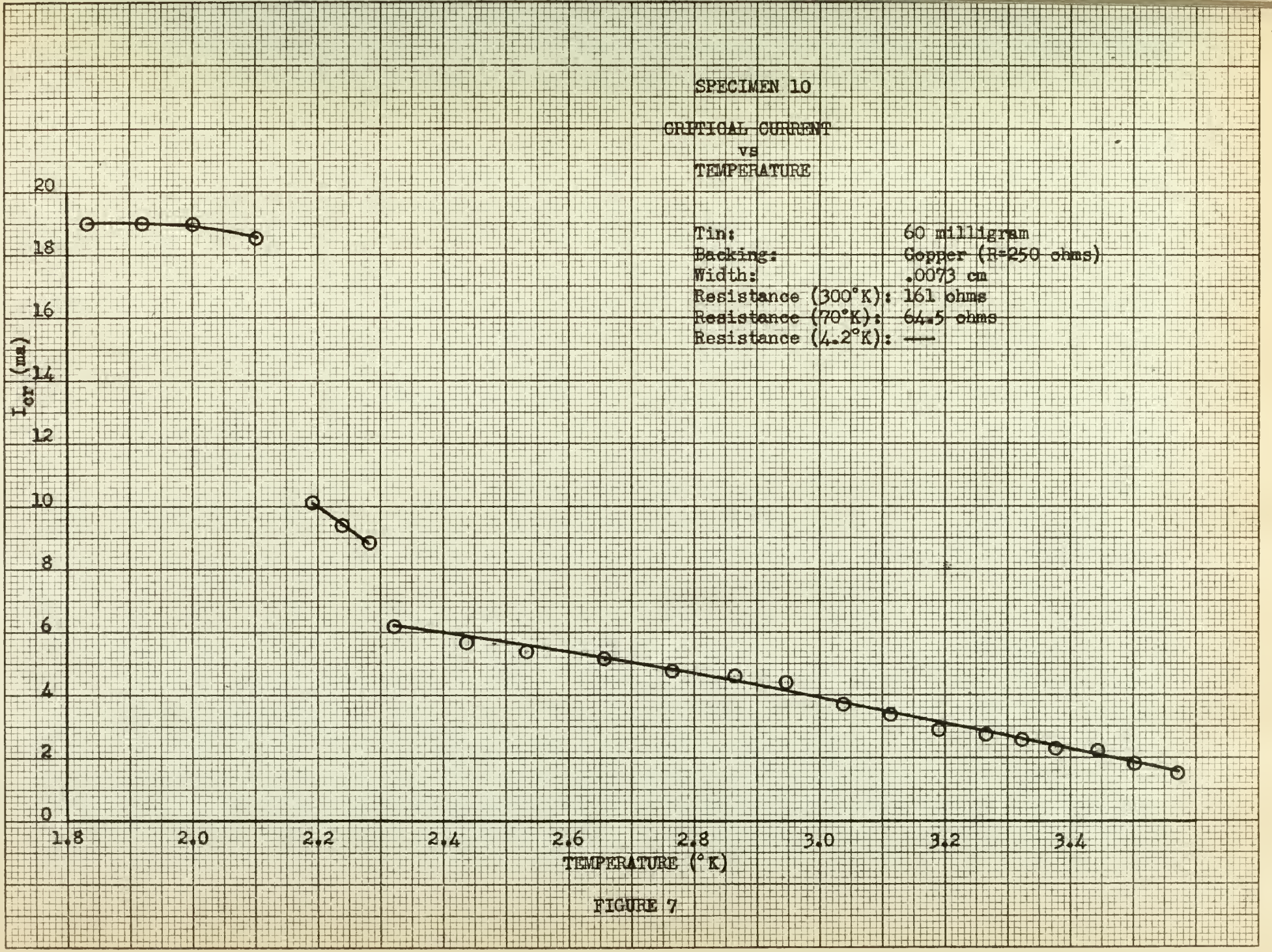

SPECIMEN 10
CRITICAL CURRENT
vs
TEMPERATURE
Tin: 60 milligram
Backing: Copper (R=250 ohms)
Width: .0073 cm
Resistance (300°K): 161 ohms
Resistance (70°K): 64.5 ohms
Resistance (4.2°K): ----
I_{cr} (ma)
0
2
4
6
8
10
12
14
16
18
20
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
TEMPERATURE (°K)

FIGURE 7

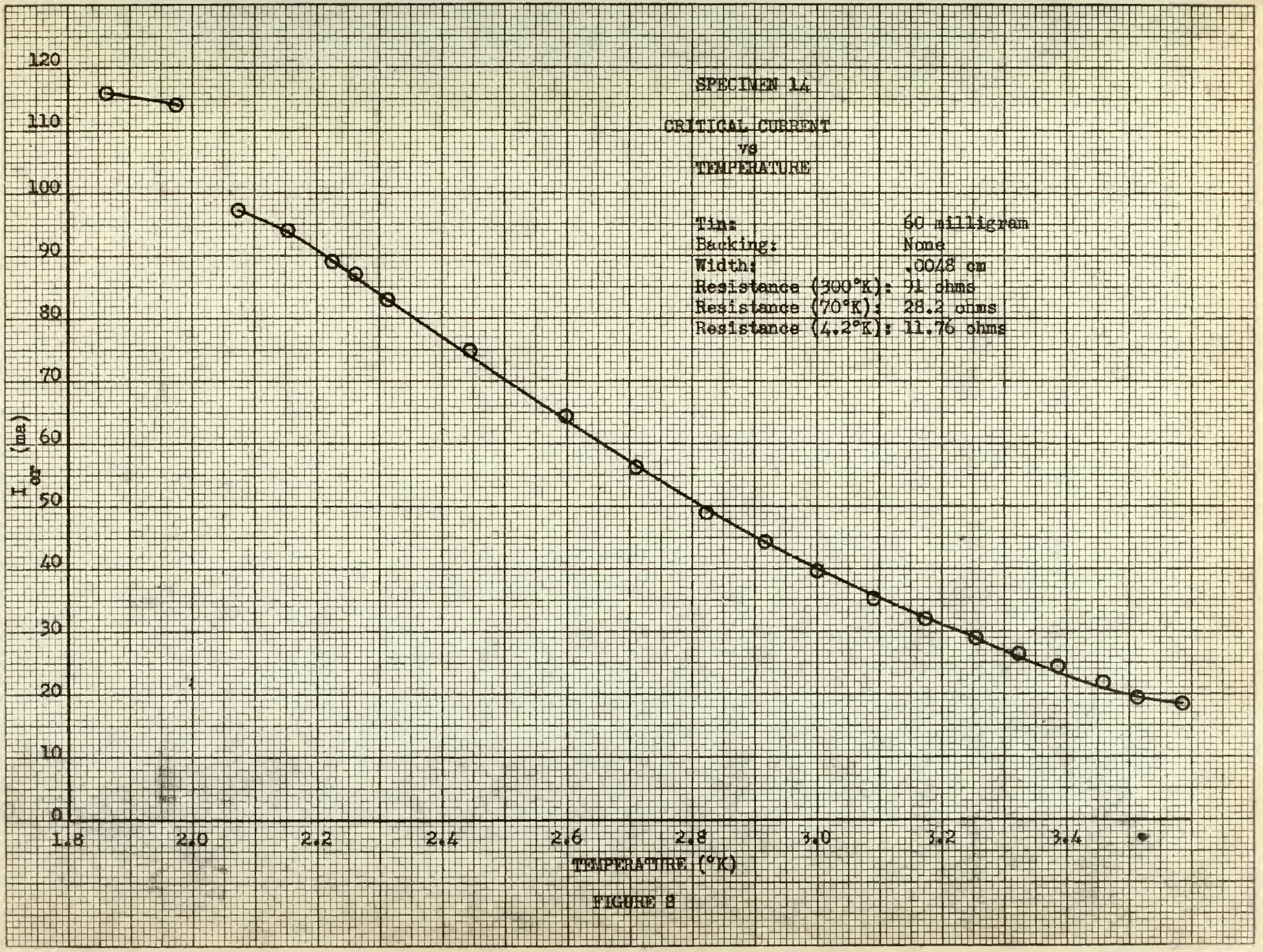

SPECIMEN 14
CRITICAL CURRENT
vs
TEMPERATURE
Tin: 60 milligram
Backing: None
Width: .0048 cm
Resistance (300°K): 91 ohms
Resistance (70°K): 28.2 ohms
Resistance (4.2°K): 11.76 ohms
I_{cr} (ma)
120
110
100
90
80
70
60
50
40
30
20
10
0
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
TEMPERATURE (°K)

FIGURE 8

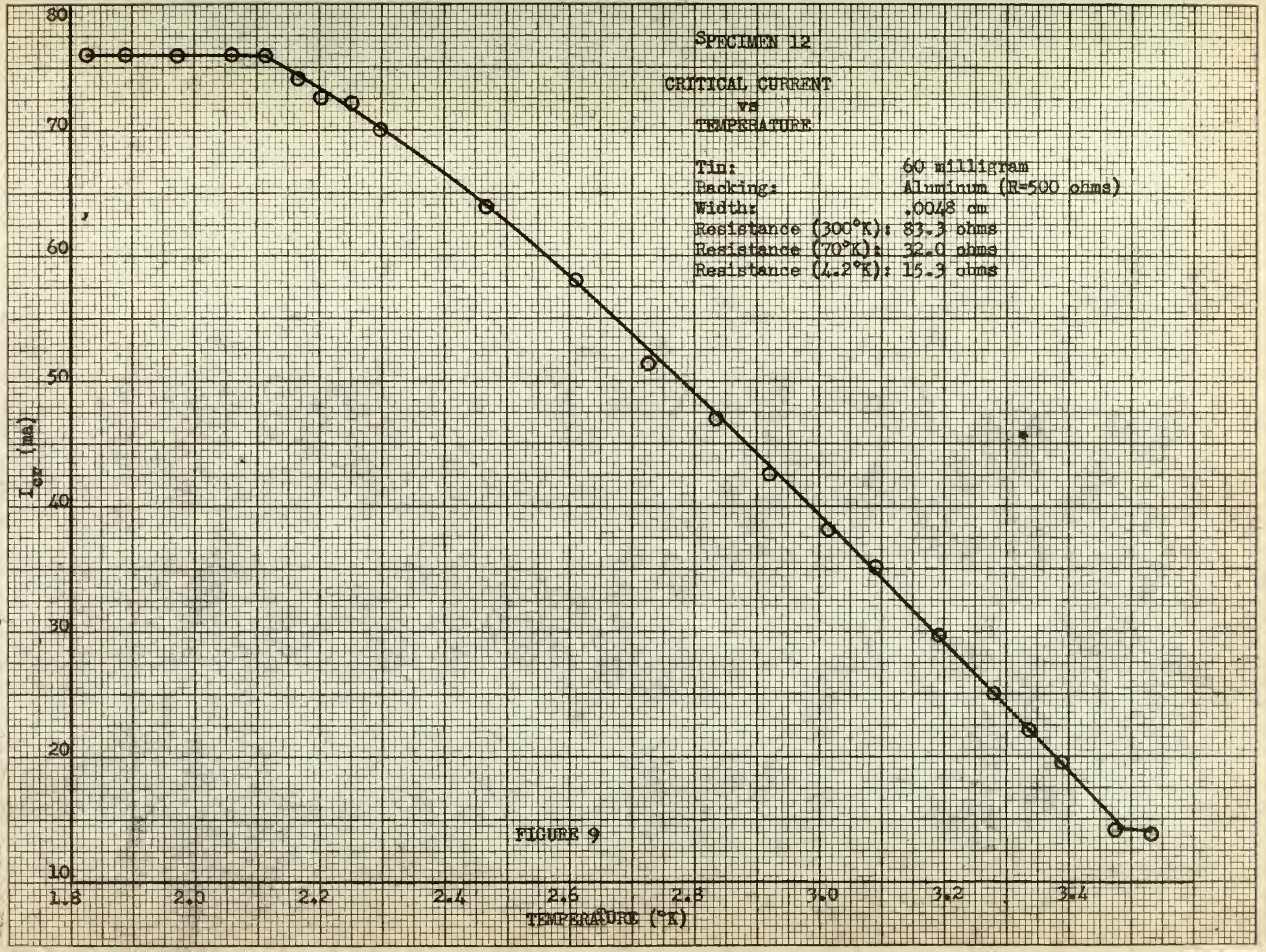

SPECIMEN 12
CRITICAL CURRENT
vs
TEMPERATURE
Tin: 60 milligram
Backing: Aluminum (R=500 ohms)
Width: .0048 cm
Resistance (300°K): 83.3 ohms
Resistance (70°K): 32.0 ohms
Resistance (4.2°K): 15.3 ohms
80
70
60
50
40
30
20
10
I_{cr} (ma)
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
TEMPERATURE (°K)

FIGURE 9

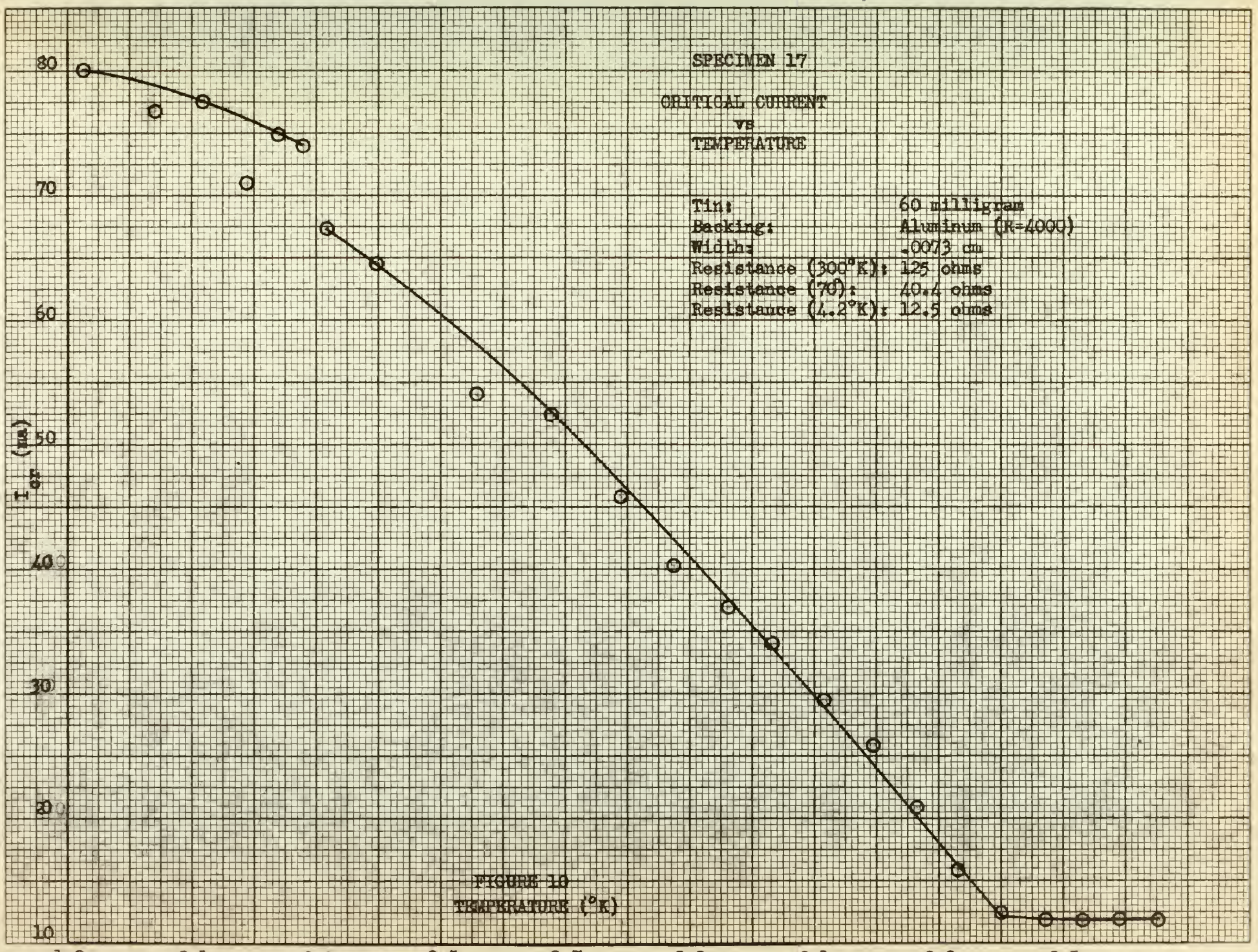
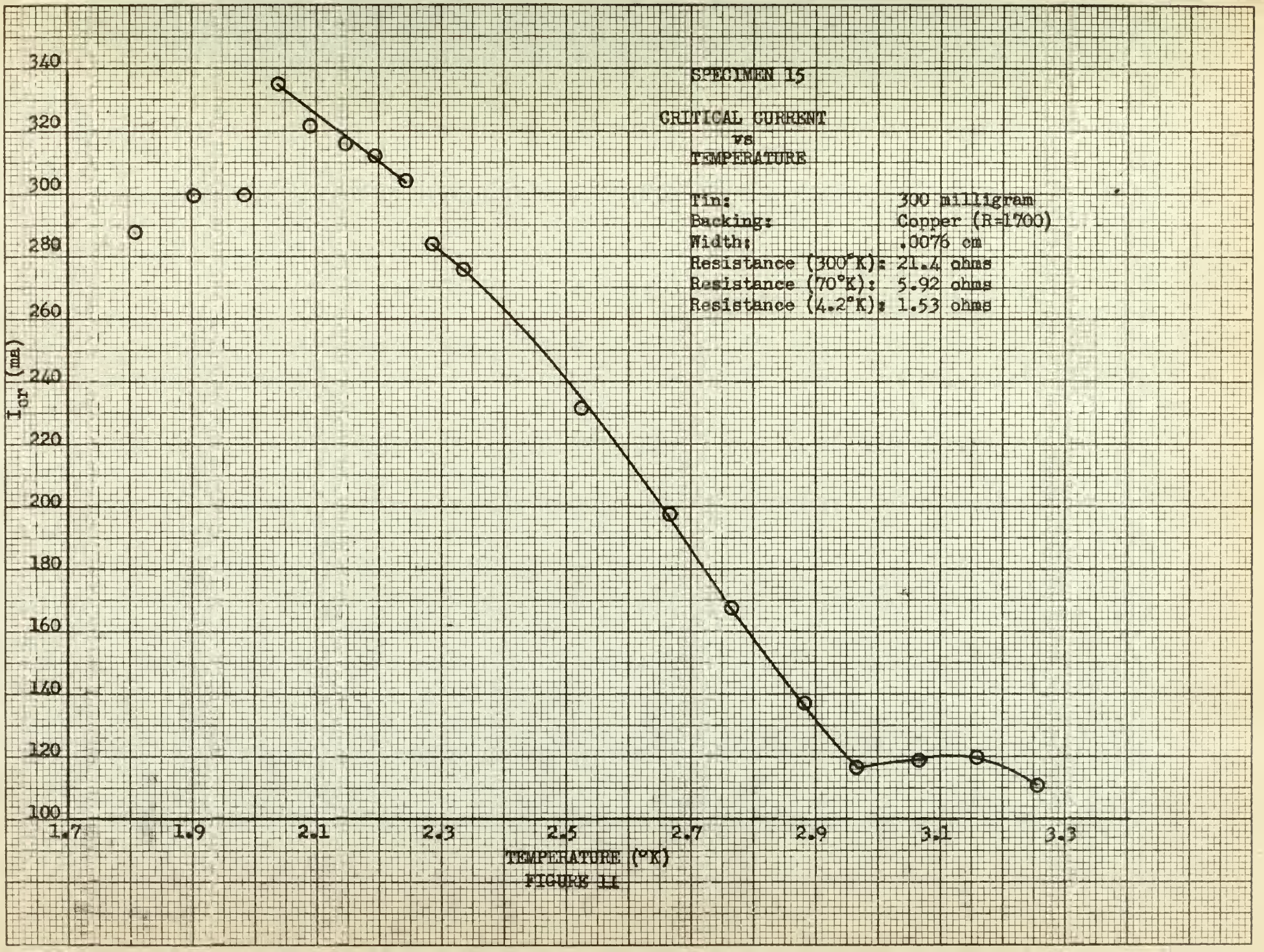

SPECIMEN 17
CRITICAL CURRENT
vs
TEMPERATURE
Tin: 60 milligram
Backing: Aluminum (R=4000)
Width: .0073 cm
Resistance (300°K): 125 ohms
Resistance (70): 40.4 ohms
Resistance (4.2°K): 12.5 ohms
80
70
60
50
40
30
20
10
1.9
2.1
2.3
2.5
2.7
2.9
3.1
3.3
3.5
TEMPERATURE (°K)

FIGURE 10


SPECIMEN 15
CRITICAL CURRENT
vs
TEMPERATURE
Tin: 300 milligram
Backing: Copper (R=1700)
Width: .0076 cm
Resistance (300°K): 21.4 ohms
Resistance (70°K): 5.92 ohms
Resistance (4.2°K): 1.53 ohms
I_{cr} (ma)
340
320
300
280
260
240
220
200
180
160
140
120
100
1.7
1.9
2.1
2.3
2.5
2.7
2.9
3.1
3.3
TEMPERATURE (°K)
FIGURE 11

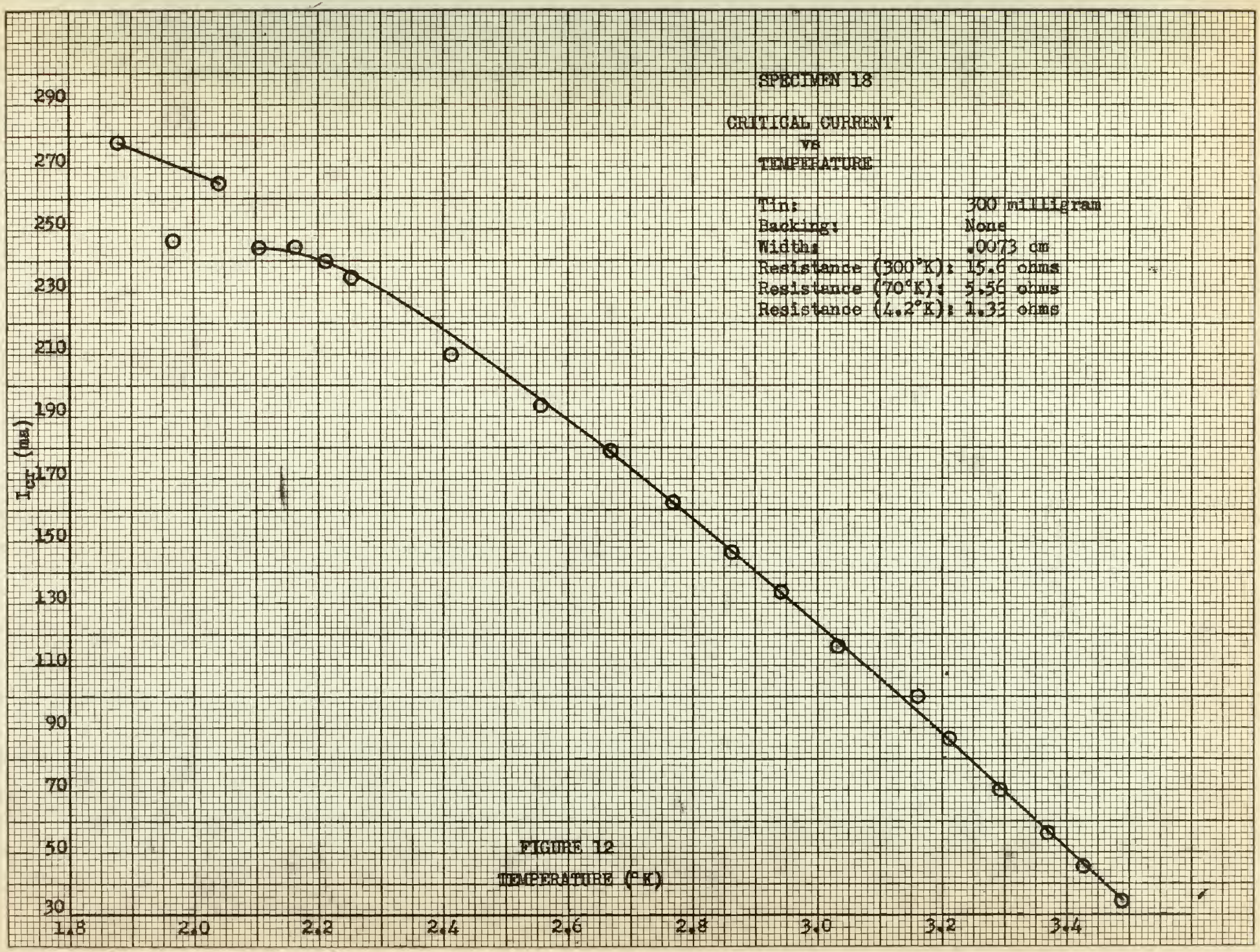

SPECIMEN 18
CRITICAL CURRENT
vs
TEMPERATURE
Tin: 300 milligram
Backing: None
Width: .0073 cm
Resistance (300°K): 15.6 ohms
Resistance (70°K): 5.56 ohms
Resistance (4.2°K): 1.33 ohms
290
270
250
230
210
190
170
150
130
110
90
70
50
30
I_{cr} (ma)
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
TEMPERATURE (°K)

FIGURE 12

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APPENDIX

TABULATED DATA

A. 60 milligram specimens.

Specimen no.:	7	11
Backing:	Copper (R = 1600 ohms)	Copper (R = 2000 ohms)
Width:	.0073 cm	.0048 cm
Resistance (300°K)	115 ohms	161 ohms
Resistance (70°K)	39.5 ohms	56.8 ohms
Resistance (4.2°K)	---	29.9 ohms

T (°K)	I_c (ma)	T (°K)	I_c (ma)
3.270	1.2	3.407	5.9
3.211	2.3	3.317	5.6
3.160	3.6	3.235	6.2
3.104	4.7	3.160	6.5
3.039	6.6	3.074	9.6
2.981	9.7	2.988	15.0
2.902	16.2	2.885	21.4
2.801	26.0	2.788	26.5
2.681	38.0	2.681	34.0
2.563	49.5	2.593	39.7
2.432	66.2	2.487	45.0
2.315	77.8	2.372	50.2
2.282	83.2	2.280	54.0
2.241	89.0	2.215	57.0
2.195	91.2	2.188	58.0
2.147	94.5	2.151	61.0
2.093	100.0	2.126	63.0
2.021	105.8	2.106	63.5
1.932	113.0	2.091	63.5
1.839	113.0	2.038	65.5
		1.989	67.0
		1.932	68.0
		1.861	71.0
		1.806	71.5
		1.787	73.0

Specimen no.:	10	14
Backing:	Copper (R = 250 ohms)	None
Width:	.0073 cm	.0048 cm
Resistance (300°K):	161 ohms	91 ohms
Resistance (70°K):	64.5 ohms	28.2 ohms
Resistance (4.2°K):	---	11.76 ohms

T (°K)	I_c (ma)	T (°K)	I_c (ma)
3.572	1.50	3.583	18.5
3.501	1.80	3.513	19.5
3.442	2.20	3.459	22.0
3.378	2.30	3.386	24.5
3.322	2.55	3.322	26.5
3.267	2.75	3.255	29.0
3.192	2.90	3.173	32.0
3.114	3.35	3.091	35.2
3.039	3.70	3.003	40.0
2.950	4.40	2.918	44.5
2.868	4.55	2.824	49.0
2.765	4.75	2.711	56.2
2.660	5.10	2.599	64.5
2.533	5.40	2.446	74.8
2.439	5.65	2.315	83.0
2.324	6.20	2.264	87.0
2.280	8.80	2.227	89.0
2.240	9.40	2.155	104.0
2.191	10.10	2.076	107.5
2.102	18.50	1.975	114.0
2.012	19.00	1.863	116.0
1.921	19.00		
1.834	19.00		
1.787	19.00		

Specimen no.:	12	17
Backing:	Aluminum (R = 500 ohms)	Aluminum (R = 4000 ohms)
Width:	.0048 cm	.0073 cm
Resistance (300°K):	83.3 ohms	125 ohms
Resistance (70°K):	32.0 ohms	40.4 ohms
Resistance (4.2°K):	15.3 ohms	12.5 ohms

T (°K)	I_c (ma)	T (°K)	I_c (ma)
3.534	13.9	3.655	12.0
3.478	14.2	3.592	12.0
3.391	19.5	3.534	12.0
3.336	22.0	3.473	12.0
3.281	25.0	3.402	12.5
3.195	29.7	3.331	16.0
3.094	35.0	3.267	21.0
2.922	42.5	3.118	29.5
2.833	47.0	3.032	34.0
2.726	51.4	2.965	37.0
2.610	58.0	2.872	40.5
2.467	63.8	2.788	46.0
2.298	70.0	2.676	52.5
2.251	72.0	2.557	54.2
2.202	72.6	2.395	64.5
2.165	74.0	2.315	67.5
2.115	76.0	2.276	74.0
2.060	75.8	2.238	75.0
1.975	76.0	2.187	71.0
1.892	76.0	2.119	77.5
1.828	78.0	2.037	77.0
		1.922	80.0
		1.892	87.0

B. 300 milligram specimens.

Specimen no.:	15	18
Backing:	Copper (R=1700 ohms)	None
Width:	.0076 cm	.0073 cm
Resistance (300°K):	21.4 ohms	15.6 ohms
Resistance (70°K):	5.92 ohms	5.56 ohms
Resistance (4.2°K):	1.53 ohms	1.33 ohms

T (°K)	I_c (ma)	T (°K)	I_c (ma)
3.253	111	3.592	35
3.160	120	3.529	46
3.067	119	3.471	57
2.969	117	3.394	71
2.881	137	3.314	87
2.765	168	3.261	100
2.665	198	3.134	116
2.526	232	3.042	134
2.332	276	2.965	146
2.285	284	2.868	162
2.241	304	2.770	179
2.196	312	2.660	194
2.146	316	2.513	215
2.091	322	2.348	235
2.039	335	2.311	240
1.983	300	2.263	244
1.903	300	2.202	244
1.808	286	2.138	265
		2.069	270
		1.977	278
		1.871	270 - 290